

Peatbog resilience to pollution and climate change over the past 2700 years in the Harz Mountains, Germany

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ABSTRACT

High-resolution plant macrofossil records were examined alongside geochemical analysis (non-destructive X-Ray fluorescence and carbon stable isotopes), pollen, and micro-charcoal data of an ombrotrophic mountain peatland located in the Harz Mountains, central Germany, Europe. We hypothesize that increased deposition of dust and pollutants across the bog surface causes changes in habitat conditions, which in turn lead to shifts in moss-dominated communities. We observe that increases in the abundance of *Sphagnum magellanicum* macrofossils – a species with a wider ecological range that occurs even in weakly minerotrophic habitats – coincide with increases of pollutant concentrations in the peat; conversely, increases of *Sphagnum rubellum* and *Sphagnum capillifolium* populations – indicators of oligotrophic conditions – coincide with decreases of pollutant concentrations. Pristine *Sphagnum* populations in the studied ombrotrophic bog have thus repeatedly returned to their original oligotrophic state (an autogenic process) following declines in pollutant input. Modern levels of pollutants should be taken into account in peatland restoration efforts, as they exert a strong control on the composition of present day *Sphagnum* communities. Moreover, *Sphagnum angustifolium* in paleoecological studies might be considered as an indicator of water level rise. In this study, the presence of *S. angustifolium* apparently correlates with wetter moisture conditions.

1. Introduction

Changes in vegetation communities in ombrotrophic bog ecosystems can be caused by allogenic (e.g., climatic and hydrological changes, fire) and autogenic (e.g. competition among local plants) factors (Barber, 1981; Charman et al., 2006; Tuittila et al., 2007; Swindles et al., 2012; Loisel and Yu, 2013; Gałka et al., 2017a). Amongst those allogenic factors, anthropogenic pollution and land use (e.g. grazing, farming, and deforestation) have been shown to directly impact bog succession and development (van Geel and Middelburg, 1988; Hölzer and Hölzer, 1998; McClymont et al., 2008; Swindles et al., 2015; Souter and Watmough, 2016). However, discerning the relative importance of autogenic, allogenic, and anthropogenic effects on ombrotrophic peatland ecosystems, and the cumulative effect of these factors on ecosystem structure and function over time, can be challenging.

Peat bogs have reliably been used as archives of past atmospheric

deposition for some elements that remain immobile in the peat stratigraphy (e.g. Shotyk, 1996; Krachler et al., 2003; Biester et al., 2012; Longman et al., 2017; Fiałkiewicz-Kozieł et al., 2018). This is because pollutants reaching ombrotrophic bogs are solely deposited via atmospheric loading (Vitt et al., 2003). That said, not every elemental concentration reflects historical deposition. For example, while dust particle inputs of zircon (Zr), titanium (Ti), and silicon (Si) tend to be immobile, mobile elements such as (earth) alkali metals (e.g., sodium (Na), calcium (Ca), magnesium (Mg)) are easily translocated or might indicate influence of minerotrophic conditions. Similarly, limiting nutrients such as nitrogen (N) and phosphorous (P) are recycled and enriched following decomposition. On the other hand, lead (Pb), mercury (Hg), and Halogens tend to bind strongly to organic matter and are thus more related to atmospheric inputs from pollution (Novak et al., 2011; Biester et al., 2012; Wang et al., 2014).

Recent studies show that even concentrations of immobile or organically bound elements in bogs are modified over time via diagenesis,

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and thus do not necessarily reflect past atmospheric deposition. While organically-bound element concentrations (e.g. Pb, Hg) might increase due to residual enrichment by mineralization processes, dust-related elements (e.g. Zr, Ti, Si, Al) are additionally affected by increasing particle density during peat decomposition (e.g. Biester et al., 2003, 2012). Therefore, changes in vegetation (e.g. from macrofossil analysis) and diagenetic processes (based on decomposition indices such as C/N) over time have to be taken into account when reconstructing past changes in pollution loading from atmospheric deposition.

Pollution can reduce *Sphagnum* populations (Gignac and Beckett, 1986; van Geel and Middelburg, 1988; Gerdol et al., 2007; McClymont et al., 2008) and has been associated with cases of *Sphagnum* disappearance (e.g. Karofeld, 1996; Paal et al., 2009). This process was first described over 200 years ago in Great Britain (Adams and Preston, 1992). Similar human impact and changes in bog plant cover – including complete disappearance – have been described over wide areas in Western Europe (Tallis, 1973; Bragg and Tallis, 2001) and North America (Gignac and Beckett, 1986; Glooschenko, 1989).

While several studies have focused on climate-influenced or human-mediated vegetation succession in bogs (e.g. Swindles et al., 2012; Gałka et al., 2017a; Kołaczek et al., 2017), only a few detailed studies have combined geochemical and ecological analyses (e.g. Jones et al., 2010; De Vleeschouwer et al., 2012; Hughes et al., 2013). Here we argue that combining those two types of analyses is necessary to better understand the effect of pollution on peat bog structure and function. We present a high-resolution plant macrofossil record combined with non-destructive X-Ray fluorescence (XRF) analysis for elemental concentrations of peat samples. We also analyzed pollen and charcoal as well as bulk peat carbon isotopes and C/N ratios. The selected ombrotrophic mountain peatland is located in the Harz region of Central Europe. This area was selected as a test case for two reasons: (1) it was a major mining region (e.g. silver, lead, copper, and zinc) for several centuries (Kempter and Frenzel, 2000, and papers cited therein), and (2) the studied peatland and others in this area have preserved their natural character despite notable human activity. The rising development of metallurgy was accompanied by deforestation, causing erosion, dust inputs, and thus enhanced deposition of lithogenic elements like Ti and Si in this region; this was accompanied by deposition of pollutants like lead (Pb) and arsenic (As) directly arising from the smelters; (Beug et al., 1999; Kempter and Frenzel, 2000). Given that concentration levels of Pb can exceed background levels by a factor up to 10,000 in this area, its presence in peat cores has been primarily linked directly to mining activity and only to a minor extent to residual enrichment from peat decomposition (Biester et al., 2012). Therefore, Pb can be used as a proxy for mining activity in the Harz region. It should be noted that such intensive activity has damaged most peatlands in many countries of Central Europe and that intact sites such as the ones reported here are very rare in this part of Europe. Indeed, the communities of *Sphagnum fuscum*, *Sphagnum cuspidatum*, *Carex limosa* and *Betula nana* that still occur in the studied bog have secured its National Park protection status (Nationalpark Harz).

We hypothesize that increased deposition of dust and pollutants across the bog surface causes changes in habitat conditions, which lead to shifts in moss-dominated communities. Specifically, we anticipate the appearance of moss species that may occur in weakly minerotrophic habitats (e.g. *Sphagnum magellanicum* and *S. russowii*) and the associated displacement of more ombrotrophic species (e.g. *Sphagnum rubellum*) following increased mineral dust inputs. We are particularly interested to determine whether such shifts in vegetation are reversed after subsequent declines of pollution inputs. The main aims of our study were thus (i) to determine the effect of pollution and human activity on plant communities in an ombrotrophic peatland of a mountainous region and (ii) to compare these effects with the influences of climate on the local plant communities in an ombrotrophic peatland in a mountain bog ecosystem.

2. Material and methods

2.1. Field sampling

Coring and sampling were performed using a 5 by 50 cm Russian peat corer. Our sampling site was in the central part of the southeastern section of the peatland, where *Sphagnum* communities are very well developed and biogeochemical studies were conducted in the past (Broder and Biester, 2015) (Fig. 1). A 377 cm-long peat profile was extracted from a lawn colonized by *Sphagnum magellanicum*, *Sphagnum rubellum*, and *Eriophorum vaginatum*. The peat was carefully inspected to avoid contamination and smearing during sampling; it was cut into 1-cm slices using surgical scissors and packed into plastic bags.

2.2. Peat core chronology

Nine Accelerator Mass Spectrometry (AMS) radiocarbon dates were measured on hand-picked plant macrofossils and used to determine peat-core chronology (App. 1). Radiocarbon dating was undertaken at the Poznań Radiocarbon Laboratory. The calibration of the radiocarbon dates and the construction of the age-depth model was performed with OxCal 4.1 (Bronk Ramsey, 2009) and the IntCal13 curve (Reimer et al., 2013) applying a P_Sequence function with a k parameter of 1 cm^{-1} and 1-cm resolution. Distinct changes in the peat composition, which might indicate a change in accumulation rates, were introduced using the “boundary” command (App. 2). The modelled ages are expressed as calendar years BC/AD.

2.3. Palaeobotanical analysis

High-resolution (1-cm peat slices) plant macrofossil analysis was used to reconstruct local plant succession. Plant macrofossils were analysed in contiguous samples of approximately 10 cm^3 . The samples were washed and sieved under a warm water current over 0.20 mesh screens. Initially, the entire sample was analysed with a stereoscopic microscope. The percentage of individual fossils of vascular plants and brown mosses was estimated, and the fossil carpological remains and vegetative fragments (leaves, rootlets, epidermis) were identified using identification keys (Smith, 2004; Mauquoy and van Geel, 2007) and compared to recently collected specimens. See Gałka et al. (2017a) for details of the methods used for plant macrofossil analysis of peats. *Sphagnum rubellum* and *S. capillifolium* were grouped together due to the difficulty of differentiating them in fossil state, particularly when stem leaves are lacking. However, these two species occur in similar habitats: both are typical ombrotrophic species that occur together in relatively dry hummocks or lawns (Rydin and McDonald, 1985; Laine et al., 2011), so in palaeoecological reconstructions they record similar environmental information. Nomenclature follows Mirek et al. (2002) for vascular plants, Ochyra et al. (2003) for bryophytes.

2.4. Pollen, non-pollen palynomorphs, and micro-charcoal analysis

Samples of 1 cm^3 at mainly 10-cm increments were prepared using the standard procedure of Erdtman's acetolysis (Berglund and Ralska-Jasiewiczowa, 1986). Analysis was carried out with an Olympus BX43 light microscope with a magnification of $600\times$; a larger magnification was used to identify problematic microremains. For taxonomical identification, pollen keys (e.g. Beug, 2004; Damske et al., 2013) and a reference collection at University of Białystok were used. Non-pollen palynomorphs (NPPs) were counted along with the pollen. The NPPs were identified using the available literature (e.g. van Geel 1978). Micro-charcoal particles were also counted and were grouped along with the pollen and were grouped into three size classes: 10–30 μm , 30–100 μm and $> 100\text{ }\mu\text{m}$ (Rull, 2009). Calculations and presentation of palynological and microcharcoal data were performed with POLPAL for Windows (Nalepka and Walanus, 2003). The arboreal pollen (AP) +

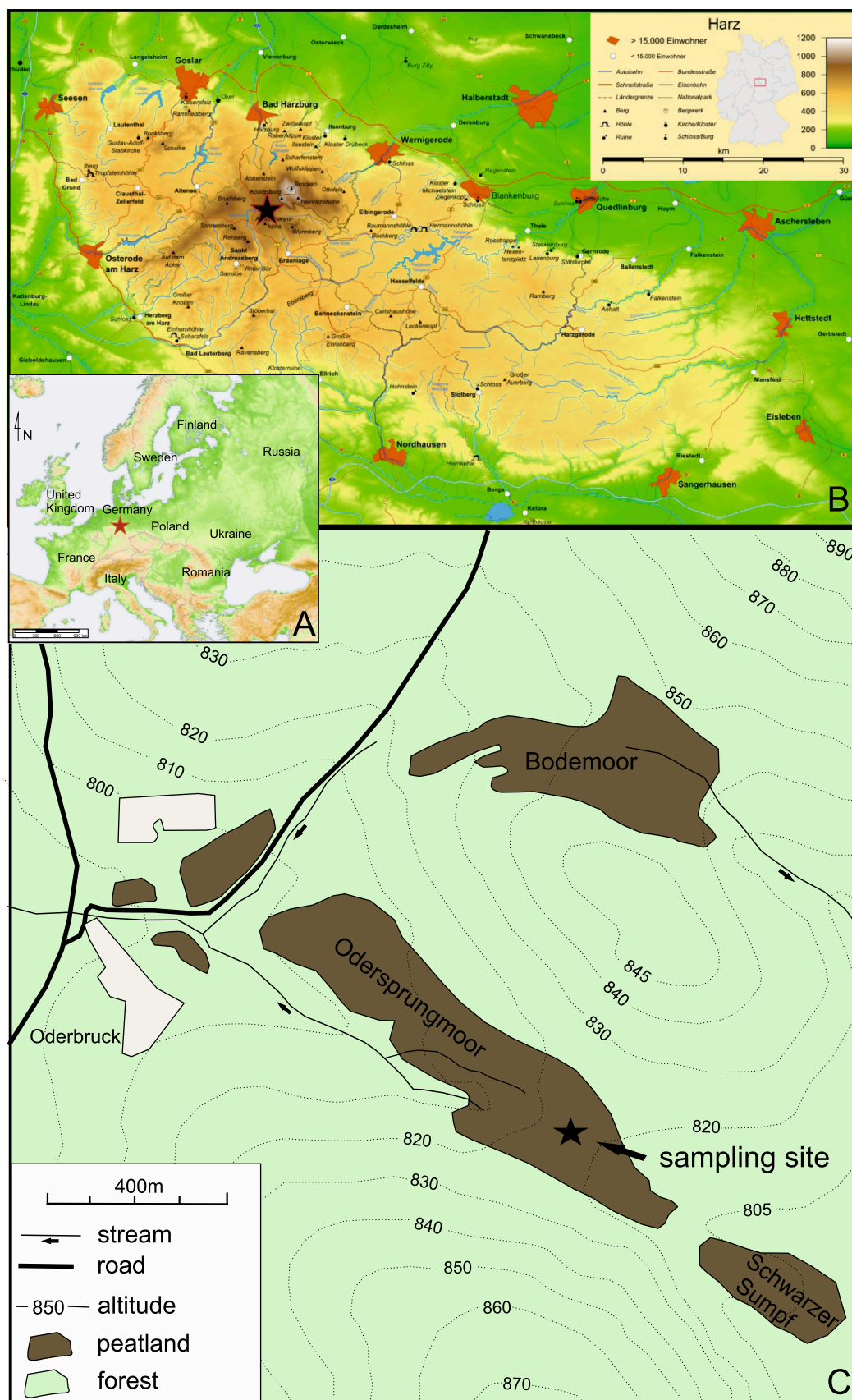


Fig. 1. Map showing locations of the two study sites in the Harz Mts. region. A) Setting within the Europe. Sampling site, asterisk; (source: http://pl.wikipedia.org/w/index.php?title=Plik:Europe_topography_map.png&filetimestamp, Author: San Jose; modified) B) Regional setting. Sampling site, asterisk (source: https://upload.wikimedia.org/wikipedia/commons/8/86/Harz_map.png) C) local setting.

non-arboreal pollen (NAP) sum was used for percentage calculations. The pollen diagram was stratigraphically ordered and zoned with constrained cluster analysis (CONISS, Grimm, 1987) and divided into local pollen assemblage zones (LPAZ). Summary curves were made for human activity indicators distinguished according to Behre (1981) and van der Linden et al. (2006).

2.5. Geochemical analysis

Geochemical analysis of the peat samples was used to reconstruct pollution and element input by atmospheric deposition (e.g. dust) over the last ca. 2700 years. Peat sample total element concentrations (Al, Ba, Br, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, P, Pb, Rb, S, Si, Sr, Ti, Zn) were determined by means of non-destructive X-Ray fluorescence spectroscopy (ZSX Primus II wavelength dispersive X-ray fluorescence spectrometer, Rigaku, Tokyo, Japan), calibrated for peat and plant material using certified reference materials.

The carbon isotopic composition ($\delta^{13}\text{C}$) of *Sphagnum* stems and *Sphagnum* dominated bulk peat was analyzed as proxies to reconstruct the local/regional environmental changes (temperature and paleohydrology). In various parts of the world, paleoecological studies have been conducted demonstrating the use of $\delta^{13}\text{C}$ in peat bogs as proxies for past conditions such as temperature, surface moisture, and/or precipitation shifts (e.g. Skrzypek and Jedrysek, 2005; Moschen et al., 2009; Loisel et al., 2010). Analyses were carried out using an elemental analyzer (EA 3000, Eurovector, Pavia, Italy) coupled to an isotope-ratio mass spectrometer (IRMS; Nu Horizon, NU Instruments, Wrexham, UK). For bulk analyses, peat was freeze-dried and milled to powder using a ZrO_2 ball mill (MM 300, Retsch, Haan, Germany). Individual, hand-picked *Sphagnum* stems were carefully dried in a drying oven at 70 °C overnight. About 4–5 mg of finely ground peat or *Sphagnum* stems of ~3 mg total weight were weighed in tin capsules for analysis. Isotope signatures of $\delta^{13}\text{C}$ are reported vs. V-PDB, as calibrated using certified reference materials and a working standard of known isotopic composition. Total concentrations of C and N in samples were also obtained from EA-IRMS analyses as described. Carbon and nitrogen concentrations are expressed based on weight-%; C/N ratios are expressed as molar C to N ratios.

2.6. Statistics and data presentation.

Standardized values (z-scores) were calculated for Si, Ti, Zn, and Pb content as well as for *Sphagnum magellanicum* percentages, to allow for statistical analysis. Pearson correlation coefficients were calculated to measure the linear correlation between these independent variables. The results are presented in the form of diagrams of plant macroremains, pollen and geochemical data (Figs. 2–4, App. 3), which were prepared with the computer program C2 (Juggins 2003).

3. Study site

Our study site, Odersprungmoor (51°46′17.53″N and 10°34′4.28″E coordinates; 800–821 m a.s.l.), is an ombrotrophic peat bog located in the Harz Mountains of Germany, in Central Europe (Fig. 1). The Harz Mountains are located southeast of Niedersachsen and southwest of Sachsen-Anhalt; they reach a maximum altitude of 1142 m a.s.l. (Mount Brocken). The High Harz Mountain area was completely glaciated during the last glacial period (Beug et al., 1999); the bedrock mainly consists of granite and quartzite (Beug et al., 1999).

Mean monthly temperature at Mount Brocken is -4.2 °C in January and 10.3 °C in July (1961–1990 monthly normals); mean annual temperature is 5 °C and total annual precipitation reaches 1814 mm (Deutscher Wetterdienst DWD). Under these modern conditions, *Picea abies* (Norway spruce) forests dominate the landscape between 500 and 1100 m a.s.l. At lower altitudes, *Fagus sylvatica* (European beech) is the dominant forest species.

All mires in the region are found on gentle slopes and saddle structures and have developed on minerogenous subsoil (Beug et al., 1999). The elongated Odersprungmoor peatland is 1100 m long and 100–300 m wide; it has an area of 27.45 ha. This peatland is located to the southeast of the village of Oderbrück (51°46′31.35″N, 10°33′43.84″E) and it directly developed on the granite bedrock (Schneekloth et al. 1983). According to Beug et al. (1999), the thickest peat layers in Odersprungmoor reach 6.6 m in the northwestern part of the bog. The central part of the Odersprungmoor is open and the vegetation of the peatland has a mosaic character. Presently, the most common plants are: *Sphagnum magellanicum*, *Sphagnum papillosum*, *Sphagnum capillifolium*, *Eriophorum vaginatum* and *Trichophorum cespitosum*; the edge of the peatland is covered with *Picea abies*. A detailed description of the vegetation at the studied peatland and other sites in the Harz Mountains is available from Beug et al. (1999) and Baumann (2009). In the northwestern part of peatland there is a pond (25 × 20 m). The Odersprungmoor bog is only weakly drained and eroded by a stream that emanates in the central part of the bog.

4. Results

4.1. Chronology, lithology, and peat accumulation rate

The age-depth model (App. 2) suggests constant accumulation rates and absence of hiatuses. The chronology assumes that no major external factors of erosion or deposition have happened in the sampled region for 2700 years, and that what is sampled at different depths is a result of periodic accumulation. The peat deposit at the Odersprungmoor was developed on the rocky bedrock and has Late Holocene origin (last 2700 years). Initially, the peat was mainly formed of *Polytrichum strictum*, followed by *Sphagnum* species (Fig. 2). The main peat-forming *Sphagnum* species are *S. magellanicum*, *S. angustifolium*, *S. rubellum*, and *S. capillifolium*. Among vascular plants *Eriophorum vaginatum* play a dominant role. The share of the brown mosses such as *Aulacomnium palustre*, *Warnstorfia fluitans*, and *Straminergon stramineum* does not exceed 30%. The peat accumulation rate was rather fast and, on average for the entire period, approximately 1.38 mm/yr and 70–140 g/m²/yr. A slower peat accumulation rate was calculated towards the bottom and upper parts where more decomposed peat with narrower C/N was documented (Fig. 4).

4.2. Local plant succession

Five zones in local vegetation development were visually delimited in the peat profile at Odersprungmoor (Fig. 2).

Zone Od-ma-1 (200–700 BC) is dominated by *Polytrichum strictum* and *Sphagnum angustifolium*. Macro-charcoal is abundant in this zone. In zone Od-ma-2 (200 BC–AD 530) *Sphagnum magellanicum* and *Eriophorum vaginatum* are the two co-dominant species. In the middle part of this zone *Carex* ssp. and *Sphagnum* cf. *auriculatum* are also present. Zone Od-ma-3 (AD 530–1070) is dominated by *Sphagnum rubellum*, *S. capillifolium* and *E. vaginatum*. An increase in *S. angustifolium* at the bottom and upper parts of this zone is also documented. *Sphagnum russowii* only appears in this zone. During zone Od-ma-4 (AD 1070–1950) *S. rubellum*, and *S. capillifolium* and *Eriophorum vaginatum* alternatively dominate the plant community. In zone Od-ma-5 (AD 1950–2015) *S. magellanicum* dominates. In the uppermost part of this most recent zone, numerous *Oxycoccus palustris* leaves are identified.

4.3. Regional plant succession

Five pollen zones, representing regional and local vegetation development, were numerically delineated in the Odersprungmoor core (App. 3).

The bottom part of the basal zone Od-po-1 (ca. 700–50 BC) is characterised by high pollen percentages of *Corylus* followed by a sharp

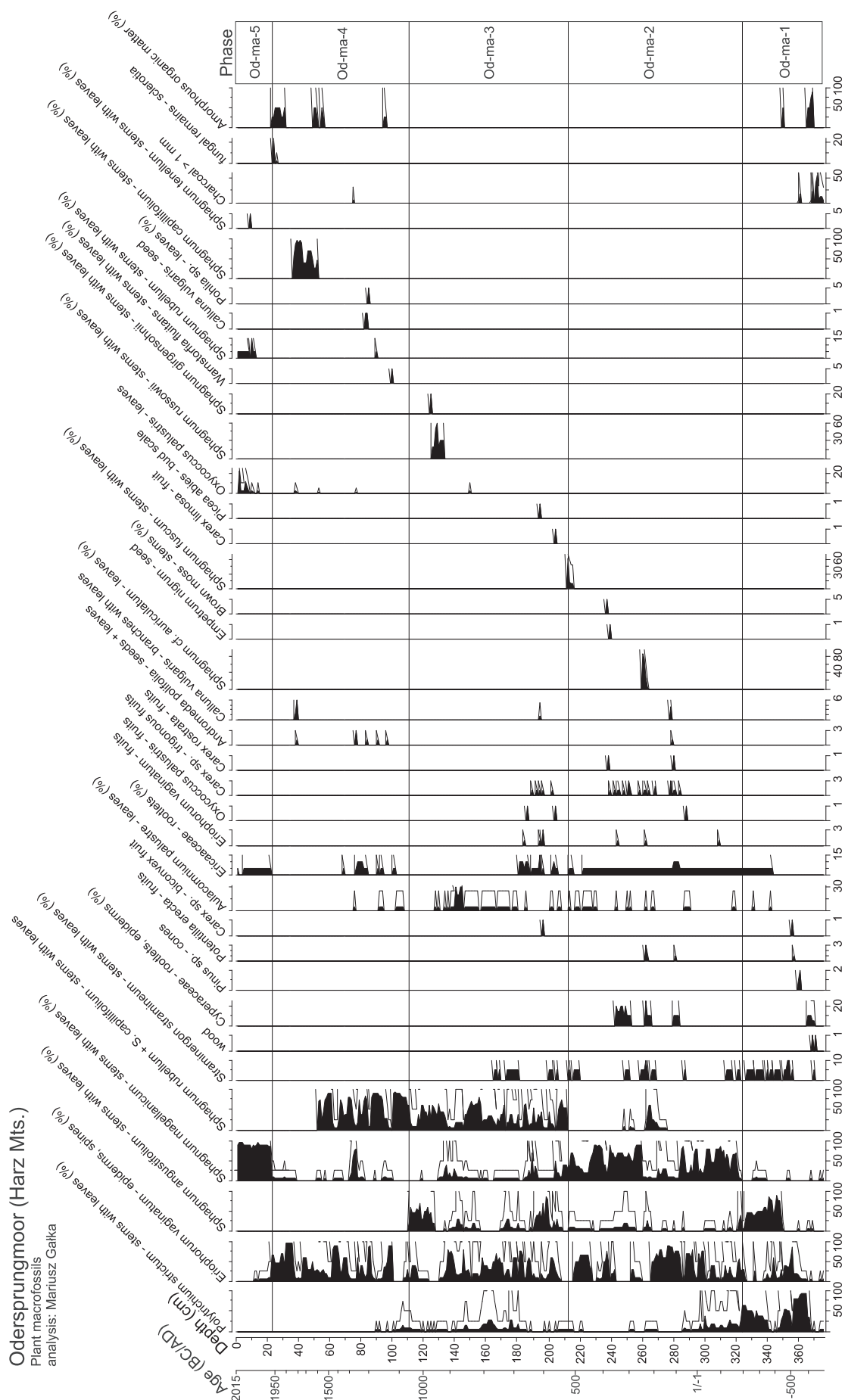


Fig. 2. Plant macrofossil diagram presenting local vegetation development in Odersprungmoor. Taxa with '%' are estimated volume percentages, the others are counts (note scale differences on the x-axes).

Odersprungmoor
geochemical analysis
analysis: Klaus-Holger Knorr

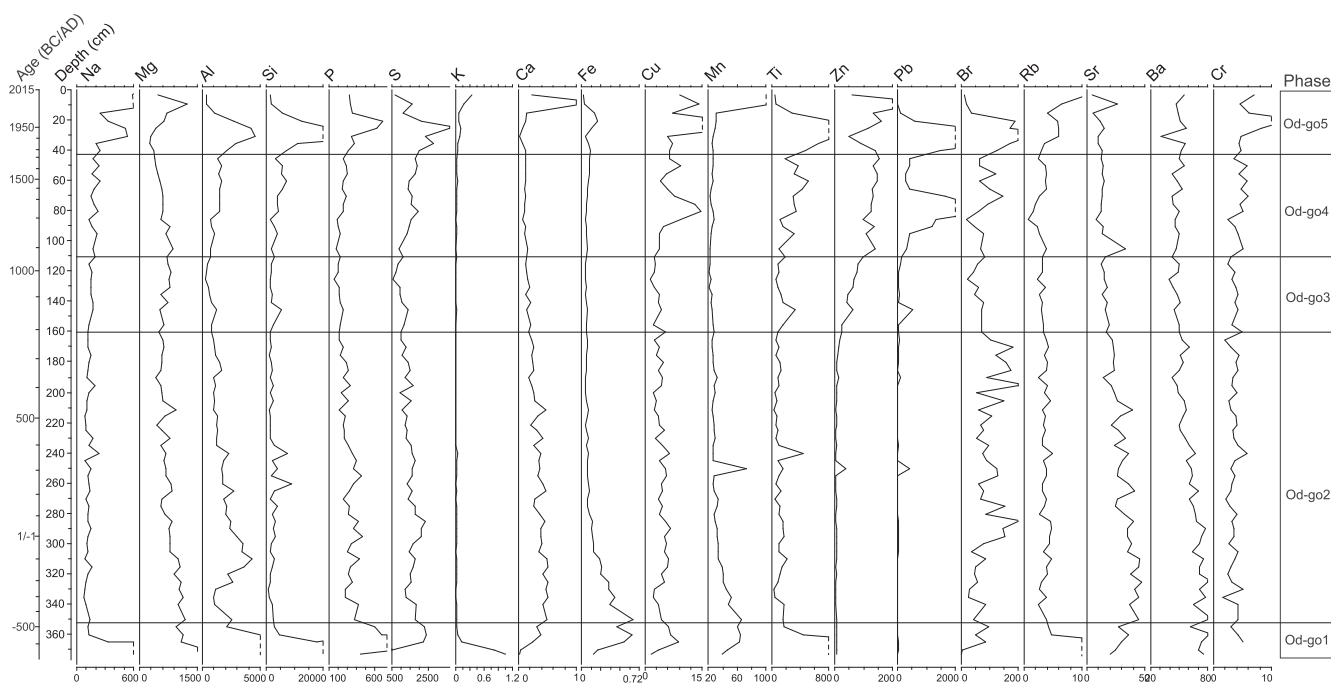


Fig. 3. Selected results of the geochemical analysis of core Odersprungmoor peatland. Results are expressed as ppm (mg/kg).

decrease. The contributions of *Pinus*, *Betula*, *Alnus*, *Quercus* and *Fagus* pollen are rather high but fluctuating, while *Carpinus* and *Picea* values remain low. Human activity indicators e.g. *Rumex acetosa/acetosella* type and *Plantago lanceolata* are present at low numbers. Copepod spermatophores are numerous, while other NPPs such as remains of *Arcella*, *Assulina*, *Habrotrocha* and *Entophlyctis lobata* increase in abundance only in the upper part of this zone. Microcharcoal particles are recorded mainly in the bottom part of this zone. Zone Od-po-2 (ca. 50 BC–300 AD) is characterised by the highest presence of Cyperaceae pollen (up to 22%). Throughout this zone there is a slight increase of *Carpinus* pollen from 1.5% to 6.5%, but overall arboreal pollen percentages show a decline. Among NPPs, fungal spores of *Tilletia sphagni* are dominant. In zone Od-po-3 (ca. AD 300–950) there is a significant increase of *Carpinus* pollen up to 15%, while *Alnus* shows a decreasing trend. Abundance of other arboreal taxa remain rather stable throughout this zone. Cyperaceae pollen percentages decrease and human activity indicators (e.g. *Plantago lanceolata* and *Cerealia*) slightly increase throughout this zone. In zone Od-po-4 (ca. AD 950–1800) values of *Alnus* and *Fagus* substantially decrease. In the middle part this zone Ericaceae pollen reach peak values of up to 33% and thereafter decrease again to 16.5%. Human activity indicators reach the highest value of the entire profile here. The upper part of this zone contains abundant micro-charcoals. Zone Od-po-5 (ca. AD 1800–2015) is characterised by a marked increase in *Picea* and *Pinus* pollen percentages, reaching peak values at the top of the zone. The proportions of *Betula*, *Alnus*, *Quercus*, *Corylus* and Ericaceae decrease substantially. Cyperaceae values increase sharply in the central part of the zone. There is a sporadic occurrence of NPPs.

4.4. Geochemical characterization

4.4.1. Major and trace elements

Elements indicating human activity (such as Pb, Zn) remain at low levels throughout zones Od-go-1 (ca. 700–450 BCE) and Od-go-2 (450 BC–AD 800) (Fig. 3).

Only small peaks occur around ca. AD 300 for various elements.

Within zone Od-go-3 (AD 800–1050), Zn and Pb, which indicate human impact, increased gradually, with a distinct peak ca. AD 850. This distinct peak was also observed for S and for other, dust related elements (e.g. Al, Si, P, Ti). In zone Od-go-4 (AD 1050–1750), Pb and Zn strongly increased; while Zn increases rather gradually, in the central part of this zone Pb concentrations show a distinct peak, even exceeding the calibrated range of 0–2000 ppm. In the uppermost zone Od-go-5 (AD 1750–2015), Pb shows a second distinct peak, again exceeding the calibrated range of up to 2000 ppm; Zn first decreases and then again strongly increases towards the top peat layers; Pb sharply decreases again after the distinct peak. Other elements related to dust deposition, such as Al, Si, P, Ti, but also Cu and S showed generally similar patterns as Pb and Zn in the upper zones Od-go-4 and Od-go-5, generally increasing towards the surface and mostly with similar distinct peaks around 20–40 cm. The peak of Pb in Od-go-4 (ca. AD 1200–1350) only co-occurred for Cu and S, and was hardly detected for other elements.

The bottom of the profile is characterized by sharp increases of Fe and Mn concentrations (600–100 BC), and particularly by a sharp increase of minerogenic elements (Ti, Si, Al, Na, P, Rb, Sr) in the downmost 20 cm. However, the decreases of Mg, Al, P, S, Ca, and Ba continue rather gradually, and elevated concentrations from zone Od-go-1 extend throughout zone Od-go-2. Lastly, redox-sensitive elements and nutrients subjected to biocycling were clearly enriched in upper peat layer (Fe, Mn, Ca, Mg, P, S).

4.4.2. C/N ratios and isotopic composition of bulk peat and Sphagnum stems

C/N ratios between ca. 700 BC and AD 700 average around 30 (Fig. 4). Between 700 and 1250 CE, C/N ratios increase and reach a maximum (93) ca. CE 1000. Thereafter, C/N ratios gradually drop to as low as 17 ca. AD 1900, and increase again in the uppermost peat layer. Bulk peat carbon isotopic composition ($\delta^{13}\text{C}$) is depleted in the heavier isotope towards the bottom part of the core (Fig. 4), reaching a maximum around 250 BC.

Carbon isotope values decrease again towards ca. CE100, followed by an increase and thereafter fluctuate without a distinct trend until

Odersprungmoor, Harz Mts.

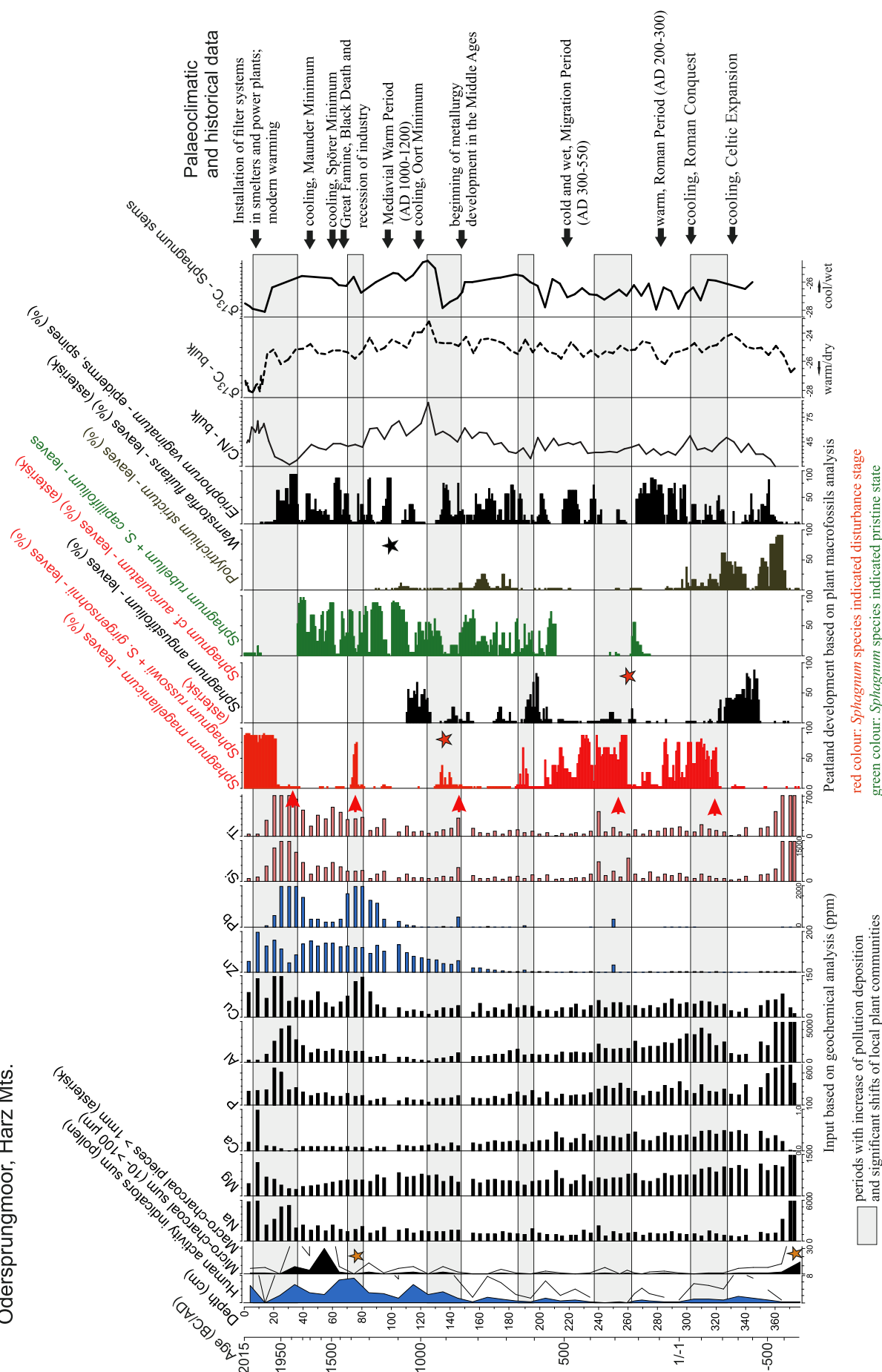


Fig. 4. Comparison of chosen taxa from pollen, micro- and macrocharcoal, plant macrofossils, and results of geochemical analysis in the Odersprungmoor peatland. Climatic data based on the Büntgen et al. (2011).

reaching a temporary maximum ca. AD 1000. Thereafter, $\delta^{13}\text{C}$ gradually decrease, reaching minima in the uppermost peat, even below values observed at the bottom of the profile.

Values of $\delta^{13}\text{C}$ in *Sphagnum* stems generally mirror trends in bulk peat $\delta^{13}\text{C}$, with some exceptions (Fig. 4). The distinct minimum ca. AD 100 in bulk peat was not as clearly reflected or even reversed in *Sphagnum* stem $\delta^{13}\text{C}$. Such opposing patterns also occur ca. AD 450–600, 1150–1350, and finally in the topmost peat. From visual inspection, values of $\delta^{13}\text{C}$ in bulk peat and *Sphagnum* particularly differ in trends in presence of larger amounts of *Eriophorum*, while values coincide well – as expected – in phases of predominance of *Sphagnum* species.

4.5. General interpretation

The covariance between the relative abundance, or even the presence/absence, of *Sphagnum magellanicum* and the amount of dust or pollution related elements (Si, Ti, Zn, and Pb) is difficult to represent statistically (App. 4).

This is despite the visually obvious coincidence between peaks in *Sphagnum magellanicum* and those from elemental abundance. The lack of significant statistical correlation between these parameters could be due to (1) the non-linear response of *Sphagnum* communities to pollution inputs, (2) the potential threshold-like response of moss communities to incremental addition of pollutants, (3) a lag in the system response time when compared to the time of deposition, which could be related to incorporation of pollutants in the water table, and (4) the interplay of other factors such as local hydroclimatic conditions, which may further influence vegetation composition (see below). Despite these difficulties and confounding factors, converting the elemental abundances to z-scores and plotting the results against the abundance of *Sphagnum magellanicum* helps with interpreting some degree of correlation between specific pollution types and sources (Fig. 4). As such, a visual examination strongly suggests the limited effect of Zn on plant communities, as the abundance of Zn has been on the rise since ~600 AD without a concomitant rise in *S. magellanicum*. Conversely, spikes in Pb seem to correspond with that of *S. magellanicum* the most.

5. Discussion

5.1. Peatland development vs. fire events, dust deposition, and human pressure

According to Beug et al. (1999) peat formation in Odersprungmoor started ca. 11,500 years ago and the present state of the peatland represents a result of merging of smaller peat bogs (mire nucleus) through lateral growth. In our sampling site the peat-forming process started ca. 700 BC, following a local fire as documented by a high amount of macro-charcoal and burned plant remains at the interface between peat and inorganic sediment ca. BC 700. According to Beug et al. (1999) deforestation did not accelerate paludification in this region; rather, the initiation of the paludification process and associated opportunity for peat-forming plants to expand is associated with fire events, as previously documented elsewhere (e.g. Tuittila et al., 2007; Schaffhauser et al., 2017). *Polytrichum strictum*, *Eriophorum vaginatum*, and *Sphagnum magellanicum* were pioneer plants that appeared on the burned soil, which was apparently still connected with local groundwater, indicated by high amounts of Na and Mg (Fig. 4), as well as P, Fe, Mn, P, and S (Fig. 3). The next fire event occurred between AD 1250 and AD 1300, coinciding well with a decrease of shrubs communities (*Ericaceae*, *Andromeda polifolia*). Shrub communities, usually occupying microsites located higher over the water level, like hummocks (Rydin, 1993), most likely had a higher potential to burn (Tuittila et al., 2007) and recovered slowly. Moreover, presence of macro-charcoal at this time coincides with increases of *S. magellanicum*. However, as our results show, the shifts to *S. magellanicum* communities may also be related to the

increase in pollution; only minor changes in C/N at such shifts indicate that these increases in pollutants were not driven by increased decomposition or residual enrichment (Biester et al., 2012). Moreover, palaeoecological studies from other sites in the world (e.g. Kuhry, 1994; Magnan et al., 2012) documented that local fire events tended not to be an important factor in modifying *Sphagnum* communities, particularly in wet ombrotrophic bogs.

Pollution from deposition of external inputs caused shifts in local plant succession, as reported previously (Hölzer and Hölzer, 1998). At Odersprungmoor, increases in dust-related elements such as Ti and Si (Biester et al., 2012), likely originating from upland mineral soils due to ongoing land clearance, triggered changes in *Sphagnum* populations ca. 200 BC, AD 250, AD 850, AD 1250, and AD 1850 (Fig. 4). During these five stages we repeatedly document increases in *S. magellanicum* populations. In contrast, we assume that periods with presence of *Sphagnum rubellum* and *S. capillifolium* populations can be considered as more pristine stages in peatland development with little external inputs related to human activities. In terms of ecological requirements, *S. magellanicum*, although common species in oligotrophic sites, has a wider ecological range and can grow even in weakly minerotrophic habitats (Hölzer, 2010; Koperski, 2011; Laine et al., 2011), thus we suggest that it was less sensible to pollution than *S. rubellum* and *S. capillifolium*. These latter species are most commonly found in more oligotrophic habitats like pristine ombrotrophic bogs (Hölzer, 2010; Laine et al., 2011). In European mountain ranges like Schwarzwald, the Western Italian Alps, and the montane area of Bulgaria, *S. magellanicum* was found in environments with pH ranging from 3.2 to values as high as 6.6 (Dierßen and Dierßen, 2001; Miserere et al., 2003; Hájková and Hájek, 2004).

The increase of Ti and Si coincides well with repeated spikes of trace metals like Zn, Pb, and Cu from mining or smelting emissions (Kempter and Frenzel, 2000; Biester et al., 2012; Fiałkiewicz-Kozieł et al., 2018). Furthermore, these peaks coincide with increases of human activity indicators such as e.g. *Cerealia*, and *Plantago lanceolata*, micro-charcoal fragments, and changes in forest ecosystems (as seen in the pollen rain). Disturbances in the forest ecosystems, decrease of *Fagus*, *Alnus* and *Carpinus* are well visible e.g. during the late Roman Period (ca. AD 150–300) and the Medieval centuries (ca. AD 950–1200) and are thus clearly associated with the increase of industrial activity that triggered deforestation (Beug et al., 1999). The first peak of Pb and Zn occurred at the Odersprungmoor site ca. AD 300, corresponding well with the first proven mining and smelting period practiced in the Harz Mountains (Kempter and Frenzel, 2000). The deforestation concomitantly increased the open surface area and increased erosional processes, consequently increasing deposition of mineral dust, as e.g. indicated by Si or Ti deposition on the peatland surface. The Si peak ca. AD 250 coincides with a short-term appearance of *Sphagnum* cf. *auriculatum* that replaced *Sphagnum rubellum/capillifolium* population at the sampling site. *Sphagnum auriculatum* is a species that can grow in more minerotrophic habitats e.g. boggy pools, acidic flushes, springs, ditches (Hölzer, 2010) and was thus likely triggered by this dust input.

The peaks in Ti and Si ca. AD 850 again coincided with a shift in *Sphagnum* communities. Here, *S. magellanicum* populations increased and subsequently *Sphagnum russowii* and *Sphagnum girgensohnii* appeared (Fig. 4). These two species, and especially *S. girgensohnii* are indicative of slight enrichment in base cations and overall increased minerotrophy (Hölzer, 2010; Laine et al., 2011). Typical base cations such as Ca or Mg could not be clearly related to the spread of these species, though; rather, silicates or associated metals related to this community change, presumably as typical base cations are more mobile and may have been translocated while immobile silicates remained as particles. Note that some trees also colonized the peatland at this time, as recorded in an increase of *Picea* pollen and in addition these species are common in the forested mires (App. 3). Our isotopic data from *Sphagnum* stems with more negative values of $\delta^{13}\text{C}$ here suggest a water level decrease or enhanced evaporation from temperature increases

(Skrzypek and Jedrysek, 2005; Moschen et al., 2009), possibly favoring the development of *Sphagnum* in dry habitats (Fig. 4).

The presence of *S. rubellum* in the uppermost peat layer (10 cm) among *S. magellanicum* populations coincides well with a decrease in dust-related elements Si and Ti. The high concentrations of Ca, Mg, and Na, but also of P and S, can likely be explained by plant uptake and recycling. These truly dissolved elements with low affinity to organic matter, and essential nutrients (such as P) get released during decomposition, which mainly takes part in the uppermost aerated peat layer. After release, they are quickly subjected to plant uptake again, which leads to an element enrichment in the uppermost peat layer (Biester et al., 2012; Wang et al., 2014). The re-appearance of *S. rubellum* indicates an improvement of the peatland site back to its natural, truly ombrotrophic character, as also reflected in again wider ratios of C/N. The particularly low values of $\delta^{13}\text{C}$ in the top layer – both in *Sphagnum* stems and bulk peat – may, however, indicate drier conditions (Skrzypek and Jedrysek, 2005).

Our results are an important message also for peatland restoration activities. We document that a *Sphagnum* population indicative of pristine, ombrotrophic conditions can repeatedly self-regenerate following lower accumulation/elimination of the pollution or dust input, which agrees with observations in Estonia, NE Europe where re-appearance of the *Sphagnum* species took place after the reduction of atmospheric pollutant input (Paal et al., 2009). Such shifts in *Sphagnum* communities may be regarded as a plasticity of bogs towards disturbance, while *Sphagnum* may only completely disappear after particular thresholds are exceeded. Moreover, the long-term ecological history of the mountain peatlands, derived from detailed, multi-proxy palaeoecological analyses (e.g. plant macrofossils, pollen, testate amoebae), might be used as a guide to inform restoration of damaged peatlands (cf. Chambers et al., 2007; McCarroll et al., 2017).

5.2. Did climate change affect plant populations at Odersprungmoor bog?

It has previously been shown that changes in plant communities in ombrotrophic peatlands can be caused by climatic changes (e.g. Barber, 1981; Mauquoy et al., 2004; Gałka et al., 2016, 2017a,b). We similarly document some shifts at Odersprungmoor that could be linked to past climatic influences, especially increases of rainfall or decreases of temperature. During cold and wet (e.g., the Migration Period, the Little Ice Age, LIA) or warm and dry (e.g., the Roman Period and the Medieval Climate Anomaly, MCA) periods in Central Europe (Büntgen et al., 2011; Moschen et al., 2009), changes in the relative abundance and presence of different mosses occurred, along with concomitant changes in values of $\delta^{13}\text{C}$ in both bulk peat and *Sphagnum*. For instance, *Warnstorfia fluitans* appeared ca. AD 1150 among a *Sphagnum rubellum/capillifolium* population for a very short time. *W. fluitans* is a typical poor-fen moss that occurs in very wet and usually acidic (pH 3.2–6.3) habitats (Hedenas, 2003). In paleoecological reconstructions, it is used as an indicator of wet conditions (Magyari et al., 2009; Dudová et al., 2012; Gałka et al., 2017b). However, such a short-term occurrence of *W. fluitans* at Odersprungmoor may indicate the appearance of a small hollow (autogenic succession) or an increase in water table (wetter climate). Our isotope record supports the second hypothesis, as values enriched in the heavier isotope suggest a thicker water film / wetter conditions (Fig. 4). Taking into account almost constant presence of *Polytrichum strictum* in periods 700 BCE–50 AD and AD 500–1200 we can infer rather low water levels at Odersprungmoor during this time period. *P. strictum* grows on the driest areas of ombrotrophic peatlands, usually on the top of hummocks (Hájková and Hájek, 2004) and water depths from ca. 15 to 65 cm below the surface (Bragazza and Gerdol, 1996).

The lack of a long-standing presence of wet-adapted plant species and communities e.g., *Sphagnum cuspidatum* or *Sphagnum balticum*, that occurring is usually interpreted in palaeoecological reconstructions as a wet climatic stage (Mauquoy et al., 2008; Gałka et al., 2017a), most

likely is associated with the form of the studied peatland that developed on the slopes. This might lead to a constant drainage of the peatland and hamper a development of very wet plant communities in the higher part of the slope and consequently disturb indicators of wetter climate stages in paleohydrological reconstructions. Such a phenomenon might also explain the rather constantly fluctuating values of $\delta^{13}\text{C}$ over long periods during peatland growth, indicating rather stable moisture conditions. Given our findings, we believe these ombrotrophic mountain peatlands developed on sloping terrain and thus wetness-related proxies have to be interpreted with care.

5.3. Role of *Sphagnum angustifolium* in local plant succession

Sphagnum angustifolium is a species often observed in mountain peatlands in Central Europe. It is especially common among *Sphagnum magellanicum* populations (e.g. Gałka et al., 2015, 2016, 2017b; Kołaczek et al., 2017). In southern Germany (Schwarzwald Mts.), *S. angustifolium* occurs most often in habitats where the water level oscillates between 3 and 17 cm below the surface (Dierßen and Dierßen, 2001). In Odersprungmoor, increases of *S. angustifolium* were accompanied by decreases in *Polytrichum strictum* (ca. 400 BC) as well *Sphagnum magellanicum*, *S. rubellum*, and *S. capillifolium* (ca. AD 600 and 1000). Based on our results and other paleoecological studies, *S. angustifolium* can be considered as a transitional species (Gałka et al., 2015, 2017a,b) that may indicate a rise in water level. This inference is based on *S. angustifolium*'s relatively smaller tolerance range for water depth whereas *S. magellanicum* is tolerant to a wide hydrological range, from dry hummocks, medium lawns, wet hollows and floating mats; it also develops extensive carpets in habitats where the water level averages 1–50 cm (Bragazza and Gerdol, 1996; Dierßen and Dierßen, 2001; Miserere et al., 2003; Hölzer, 2010). *Sphagnum rubellum* and *S. capillifolium* mainly occur in oligotrophic habitats in the driest parts of peatland, on the hummocks (Hölzer, 2010; Wojtuń et al., 2013).

The relationship between the emergence of *S. angustifolium* populations and the increase in the water level may be partially supported by the results of isotopic studies. The growth of *S. angustifolium* usually coincided with less negative (higher) $\delta^{13}\text{C}$ values (Fig. 4). Thereby, higher $\delta^{13}\text{C}$ values correspond to more humid and/or cooler climatic conditions (Skrzypek and Jedrysek, 2005).

6. Conclusions

The long-term ecological history of the Odersprungmoor peat profile allowed us to reconstruct palaeoenvironmental changes during the last ~2700 years in the Harz Mts. region. From our study we conclude:

1. That a *Sphagnum* population indicative of pristine, ombrotrophic conditions can repeatedly self-regenerate as an autogenic process after decreased input of pollutants and dust related elements. We thus believe that, information from such multi-proxy detailed palaeoecological analyses, is particularly useful for restoration of damaged peatlands to understand potential vegetation communities at present stage.
2. That palaeohydrological reconstructions benefit from complementary approaches, including vegetation and other proxies such as isotope analysis, as ombrotrophic mountain bogs developing on slopes may not develop typical patterns of wetness indicators.
3. *Sphagnum angustifolium* can be considered a transitional species, whose appearance and especially increase of the population may partly indicate a rise in water level.

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Appendix A. Supplementary data

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References

- Adams, K.J., Preston, C.D., 1992. Evidence for the effects of atmospheric pollution on bryophytes from national and local recording. In: Harding, P.T. (Ed.), *Biological Recording of Changes in British Wildlife*. The Stationery Office, London, pp. 31–43.
- Barber, K.E., 1981. Peat Stratigraphy and Climatic Change. A Palaeoecological Test of the Theory of Cyclic Bog Regeneration. A. A. Balkema, Rotterdam, NL.
- Baumann, K., 2009. Entwicklung der Moorvegetation im Nationalpark Harz. Band 4. Schriftenreihe aus dem Nationalpark Harz, Wernigerode.
- Behre, K.-E., 1981. The interpretation of anthropogenic indicators in pollen diagrams. *Pollen Spores* 23, 225–245.
- Berglund, B.E., Ralska-Jasiewiczowa, M., 1986. Pollen analyses and pollen diagrams. In: Berglund, B.E. (Ed.), *Handbook of Holocene Palaeoecology and Palaeohydrology*. John Wiley, Chichester, pp. 455–484.
- Beug, H.J., 2004. Leitfaden der Pollenbestimmung für Mitteleuropa und angrenzende Gebiete. Pfeil, München.
- Beug, H.-Jürgen, Henrion, I., Schmäser, A., 1999. Landschaftsgeschichte im Hochharz. Die Entwicklung der Wälder und Moore seit dem Ende der letzten Eiszeit. Gesellschaft zur Förderung des Nationalparks Harz e.V., Goslar.
- Biester, H., Martinez-Cortizas, A., Birkenstock, S., Kilian, R., 2003. Effect of peat decomposition and mass loss on historic mercury records in peat bogs from Patagonia. *Environ. Sci. Technol.* 37, 32–39.
- Biester, H., Hermanns, Y.-M., Martinez-Cortizas, A., 2012. The influence of organic matter decay on the distribution of major and trace elements in ombrotrophic mires – a case study from the Harz Mountains. *Geochim. Cosmochim. Acta* 84, 126–136.
- Bragg, O.M., Tallis, J.H., 2001. The sensitivity of peat-covered upland landscapes. *Catena* 42, 345–360.
- Bragazza, L., Gerdol, R., 1996. Response surfaces of plant species along water-table depth and pH gradients in a poor mire on the southern Alps (Italy). *Ann. Bot. Fenn.* 33, 11–20.
- Broder, T., Biester, H., 2015. Hydrologic controls on DOC, As and Pb export from a polluted peatland – the importance of heavy rain events, antecedent moisture conditions and hydrological connectivity. *Biogeosciences* 12, 4651–4664.
- Bronk Ramsey, C., 2009. Bayesian analysis of radiocarbon dates. *Radiocarbon* 51, 337–360.
- Büntgen, U., Tegel, W., Nicolussi, K., McCormick, M., Frank, D., Trouet, V., Kaplan, J.O., Herzig, F., Heussner, K.-U., Esper, J., 2011. 2500 years of European climate variability and human susceptibility. *Science* 331, 578–582.
- Chambers, F.M., Mauquoy, D., Gent, A., Pearson, F., Daniell, J.R.G., Jones, P.S., 2007. Palaeoecology of degraded blanket mire in South Wales: data to inform conservation management. *Biol. Conserv.* 137, 197–209.
- Charman, D.J., Blundell, A., Chiverrell, R.C., Hendon, D., Langdon, P.G., 2006. Compilation of non-annually resolved Holocene proxy climate records: stacked Holocene peatland palaeo-water table reconstructions from northern Britain. *Quat. Sci. Rev.* 25, 336–350.
- Demske, D., Tarasov, P.E., Nakagawa, T., 2013. Atlas of pollen, spores and further non-pollen palynomorphs recorded in the glacial-interglacial late Quaternary sediments of Lake Suigetsu, central Japan. *Quart. Int.* 290, 164–238.
- Vleeschouwer, De, Pazdur, A., Luthers, C., Stree, M., Mauquoy, D., Wastiaux, C., Le Roux, G., Moschen, R., Blaauw, M., Pawlyta, J., Sikorski, J., Piotrowska, N., 2012. A millennial record of environmental change in peat deposits from the Misten bog (East Belgium). *Quart. Int.* 268, 44–57.
- Dierßen, K., Dierßen, B., 2001. Moore. Ulmer, Stuttgart.
- Dudová, L., Hájková, P., Buchtová, H., Opravilová, V., 2012. Formation, succession and landscape history of Central-European summit raised bogs: a multiproxy study from the Hrubý Jeseník Mountains. *Holocene* 23, 230–242.
- Fiałkiewicz-Koziele, B., De Vleeschouwer, F., Mattioli, N., Fageld, N., Palowski, B., Pazdur, A., Smieja-Król, B., 2018. Record of Anthropocene pollution sources of lead in disturbed peatlands from Southern Poland. *Atmos. Environ.* 179, 61–68.
- Gałka, M., Miotk-Szpiganowicz, G., Marczevska, M., Barabach, J., van der Knaap, W.O., Lamentowicz, M., 2015. Palaeoenvironmental changes in Central Europe (NE Poland) during the last 6200 years reconstructed from a high resolution multi-proxy peat archive. *Holocene* 25, 421–434.
- Gałka, M., Tantau, I., Ersek, V., Feurdean, A., 2016. A 9000 year record of cyclic vegetation changes identified in a montane peatland deposit located in the Eastern Carpathians (Central-eastern Europe): autogenic succession or regional climatic influences? *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 449, 52–61.
- Gałka, M., Tantau, I., Feurdean, A., 2017a. Plant succession in a peatland in the Eastern Carpathian Mts. (CE Europe) during the last 10,200 years: Implications for peatland development and palaeoclimatic research. *Rev. Palaeobot. Palynol.* 244, 203–216.
- Gałka, M., Tobolski, K., Lamentowicz, L., Ersek, V., Jassey, V.E.J., van der Knaap, W.O., Lamentowicz, M., 2017b. Unveiling exceptional Baltic bog ecohydrology, autogenic succession and climate change during the last 2000 years in CE Europe using replicate cores, multi-proxy data and functional traits of testate amoebae. *Quat. Sci. Rev.* 156, 90–106.
- Gerdol, R., Petraglia, A., Bragazza, L., Iacumin, P., Brancaloni, L., 2007. Nitrogen deposition interacts with climate in affecting production and decomposition rates in *Sphagnum* mosses. *Global Change Biol.* 13, 1810–1821.
- Gignac, L.D., Beckett, P.J., 1986. The effect of smelting operations on peatlands near Sudbury, Ontario, Canada. *Can. J. Bot.* 64, 1138–1147.
- Glooschenko, W.A., 1989. *Sphagnum fuscum* moss as an indicator of atmospheric deposition across Canada. *Environ. Pollut.* 57, 27–33.
- Grimm, E.C., 1987. CONISS: a Fortran 77 program for stratigraphically constrained cluster analysis by the method of incremental sum of squares. *Comput. Geosci.* 13, 13–35.
- Hájková, P., Hájek, M., 2004. Bryophyte and vascular plant responses to base-richness and water level gradients in western Carpathian *Sphagnum*-rich mires. *Folia Geobot.* 39, 335–351.
- Hedenas, L., 2003. The European species of the *Calliergon-Scorpidium-Drepanocladus* complex, including some related or similar species. *Meylania* 28, 1–116.
- Hölzer, A., 2010. Die Torfmoose Südwestdeutschlands und der Nachbargebiete. Weissdorn Verlag Jena, Jena.
- Hölzer, A., Hölzer, A., 1998. Silicon and titanium in peat profiles as indicators of human impact. *Holocene* 8, 685–696.
- Hughes, P.D.M., Mallon, G., Brown, A., Essex, H.J., Stanford, J.D., Hotes, S., 2013. The impact of high tephra loading on late-Holocene carbon accumulation and vegetation succession in peatland communities. *Quat. Sci. Rev.* 67, 160–175.
- Jones, M.C., Peteet, D.M., Sambrotto, R., 2010. Late-glacial and Holocene d15N and d13C variation from a Kenai Peninsula, Alaska peatland. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 293, 132–143.
- Juggins, S., 2003. C2 User Guide. Software for Ecological and Palaeoecological Data Analysis and Visualisation. University of Newcastle, Newcastle upon Tyne, UK.
- Karofeld, E., 1996. The effects of alkaline fly ash precipitation on the *Sphagnum* mosses in Niinsaare bog, NE Estonia. *Suo* 47, 105–114.
- Kempton, H., Frenzel, B., 2000. The impact of early mining and smelting on the local tropospheric aerosol detected in ombrotrophic peat bogs in the Harz, Germany. *Water, Air Soil Pollut.* 121, 93–108.
- Kolaczek, P., Karpińska-Kolaczek, M., Marcisz, K., Gałka, M., Lamentowicz, M., 2017. Palaeohydrology and the human impact on one of the largest raised bogs complex in the Western Carpathians (Central Europe) during the last two millennia. *Holocene* 28, 595–608.
- Koperski, M., 2011. Die Moose des Nationalparks Harz. Eine kommentierte Artenliste. Band 8. Schriftenreihe aus dem Nationalpark Harz, Wernigerode.
- Krachler, M., Mohl, C., Emons, H., Shoty, W., 2003. Atmospheric deposition of V, Cr, and Ni since the late glacial: Effects of climatic cycles, human impacts, and comparison with crustal abundances. *Environ. Sci. Technol.* 37, 2658–2667.
- Kuhry, P., 1994. The role of fire in the development of *Sphagnum*-dominated peatlands in western Boreal Canada. *J. Ecol.* 82, 899–910.
- Laine, J., Harju, P., Timonen, T., Laine, A., Tuittila, E.-S., Minkinen, K., Vasander, H., 2011. The Intricate Beauty of *Sphagnum* Mosses – A Finnish Guide to Identification. University of Helsinki Department of Forest Sciences Publications 2.
- Loisel, J., Garneau, M., Helie, J.F., 2010. *Sphagnum* δ13C values as indicators of palaeohydrological changes in a peat bog. *Holocene* 20, 285–291.
- Loisel, J., Yu, Z., 2013. Surface vegetation patterning controls carbon accumulation in peatlands. *Geophys. Res. Lett.* 40, 1–6.
- Longman, J., Veres, D., Ersek, V., Salzmann, U., Hubay, K., Bormann, M., Wennrich, V., Schäbitz, F., 2017. Periodic input of dust over the Eastern Carpathians during the Holocene linked with Saharan desertification and human impact. *Clim. Past* 13, 897–917.
- Magnan, G.M., Lavoie, M., Payette, S., 2012. Impact of fire on long-term vegetation dynamics of ombrotrophic peatlands in northwestern Quebec, Canada. *Quat. Res.* 77, 110–121.
- Magyari, E.K., Buczkó, K., Jakab, G., Braun, M., Pál, Z., Karátson, D., Papp, P., 2009. Palaeolimnology of the last crater lake in the Eastern Carpathian Mountains – a multiproxy study of Holocene hydrological changes. *Hydrobiologia* 631, 29–63.
- Mauquoy, D., van Geel, B., 2007. Mire and peat macros. In: Elias, S.A. (Ed.), *Encyclopedia of Quaternary Science*. Elsevier, Amsterdam, pp. 2315–2336.
- Mauquoy, D., Yeloff, D., van Geel, B., Charman, D., Blundell, A., 2008. Two decadal resolved records from north-west European peat bogs show rapid climate changes associated with solar variability during the mid-late Holocene. *J. Quat. Sci.* 23, 745–763.
- Mauquoy, D., van Geel, B., Blaauw, M., Speranza, A., van der Plicht, J., 2004. Changes in solar activity and Holocene climatic shifts derived from 14C wiggle-match dated peat deposits. *Holocene* 14, 45–52.
- McCarroll, J., Chambers, F.M., Webb, J.C., Thom, T., 2017. Application of palaeoecology for peatland conservation at Mossdale Moor, UK. *Quart. Int.* 432, 39–47.
- McClymont, E.L., Mauquoy, D., Yeloff, D., Broekens, P., van Geel, B., Charman, D.J., Pancost, R.D., Chambers, F.P., Evershed, R.P., 2008. The disappearance of *Sphagnum imbricatum* from butterburn flow, UK. *Holocene* 18, 991–1002.

- Mirek, Z., Piękoś-Mirkowa, H., Zając, A., Zając, M., 2002. Flowering Plants and Peridophytes of Poland. A Checklist. IB PAN, Kraków.
- Miserere, L., Montacchini, F., Buffa, G., 2003. Ecology of some mire and bog plant communities in the western Italian Alps. *J. Limnol.* 62, 88–96.
- Moschen, R., Kuhl, N., Rehberger, I., Lücke, A., 2009. Stable carbon and oxygen isotopes in sub-fossil *Sphagnum*: assessment of their applicability for palaeoclimatology. *Chem. Geol.* 259, 262–272.
- Nalepka, D., Walanus, A., 2003. Data processing in pollen analysis. *Acta Palaeobot.* 43, 125–134.
- Novak, M., Zemanova, L., Voldrichova, P., Stepanova, M., Adamova, M., Pacheroova, P., Komarek, A., Krachler, M., Prechova, E., 2011. Experimental evidence for mobility/immobility of metals in peat. *Environ. Sci. Technol.* 45, 7180–7187.
- Ochyra, R., Żarnowiec, J., Bednarek-Ochyra, H., 2003. In: *Census Catalogue of Polish Mosses*. W. Szafer Institute of Botany. Polish Academy of Sciences, pp. 372.
- Paal, J., Vellak, K., Liira, J., Karofeld, E., 2009. Bog recovery in northeastern Estonia after the reduction of atmospheric pollution input. *Restor. Ecol.* 18, 387–400.
- Reimer, P.J., Bard, E., Bayliss, A., Beck, J.W., Blackwell, P.G., Bronk Ramsey, C., Buck, C.E., Cheng, H., Edwards, R.L., Friedrich, M., Grootes, P.M., Guilderson, T.P., Hafflidason, H., Hajdas, I., Hatt, C., Heaton, T.J., Hoffmann, D.L., Hogg, A.G., Hughen, K.A., Kaiser, K.F., Kromer, B., Manning, S.W., Niu, M., Reimer, R.W., Richards, D.A., Scott, E.M., Southon, J.R., Staff, R.A., Turney, C.S.M., van der Plicht, J., 2013. Intcal13 and Marine13 radiocarbon age calibration curves 0–50,000 years cal BP. *Radiocarbon* 55, 1869–1887.
- Rull, V., 2009. New palaeoecological evidence for the potential role of fire in the Gran Sabana, Venezuelan Guayana, and implications for early human occupation. *Veg. Hist. Archaeobot.* 18, 219–224.
- Rydin, H., 1993. Mechanism of interactions among *Sphagnum* species along water-level gradients. *Adv. Bryol.* 5, 153–185.
- Rydin, H., McDonald, A.J.S., 1985. Tolerance of *Sphagnum* to water level. *J. Bryol.* 13, 571–578.
- Schaffhauser, A., Payette, S., Garneau, M., Robert, E.C., 2017. Soil paludification and *Sphagnum* bog initiation: the influence of indurated podzolic soil and fire. *Boreas* 46, 428–441.
- Schneekloth, H., Jensen, U., Beug, H.-J., 1983. Die Moore in Niedersachsen, 8. Teil. Bd 96, H. 8. Veröff. Nieders. Inst. Landeskunde u. Landesentwicklung, Reihe A Forsch. Landes- und Volkskunde, Göttingen.
- Shotyk, W., 1996. Peat bog archives of atmospheric metal deposition: Geochemical evaluation of peat profiles, natural variations in metal concentrations, and metal enrichment factors. *Environ. Rev.* 4, 149–183.
- Skrzypek, G., Jedrysek, M.-O., 2005. 13C/12C ratio in peat cores: record of past climates. In: Lichtfouse, E., Schwarzbauer, J., Didier, R. (Eds.), *Environmental Chemistry*. Springer, Berlin, pp. 65–73.
- Smith, A.J.E., 2004. *The Moss Flora of Britain and Ireland*. Cambridge University Press, Cambridge.
- Souter, L., Watmough, S.A., 2016. The impact of drought and air pollution on metal profiles in peat cores. *Sci. Total Environ.* 541, 1031–1040.
- Swindles, G.T., Morris, P.J., Baird, A.J., Blaauw, M., Plunkett, G., 2012. Ecohydrological feedbacks confound peat-based climate reconstructions. *Geophys. Res. Lett.* 39, L11401.
- Swindles, G.T., Turner, T.E., Roe, H.M., Hall, V.A., Rea, H.A., 2015. Testing the cause of the *Sphagnum austini* (Sull. ex Aust.) decline: multiproxy evidence from a raised bog in Northern Ireland. *Rev. Palaeobot. Palynol.* 213, 17–26.
- Tallis, J.H., 1973. The terrestrialization of lake basins in north Cheshire with special reference to the development of a “schwingmoor” structure. *J. Ecol.* 61, 537–567.
- Tuittila, E.-S., Valiranta, M., Laine, J., Korhola, A., 2007. Quantifying patterns and controls of mire vegetation succession in a southern boreal bog in Finland using partial ordinations. *J. Veg. Sci.* 18, 891–902.
- van der Linden, M., Vickery, E., Charman, D.J., Broekens, P., van Geel, B., 2006. Vegetation history and human impact during the last 300 years recorded in a German peat deposit. *Rev. Palaeobot. Palyn.* 152, 158–175.
- van Geel, B., 1978. A palaeoecological study of Holocene peat bog sections in Germany and the Netherlands, based on the analysis of pollen, spores and macro- and microscopic remains of fungi, algae, cormophytes and animals. *Rev. Palaeobot. Palynol.* 25, 1–120.
- van Geel, B., Middelorp, A.A., 1988. Vegetational history of Carbury Bog (Co. Kildare, Ireland) during the last 850 years and a test of the temperature indicator value of 2H/1H measurements of peat samples in relation to historical sources and meteorological data. *New Phytol.* 109, 377–392.
- Vitt, D., Wieder, R.K., Halsey, L., Turetsky, M., 2003. Response of *Sphagnum fuscum* to nitrogen deposition: a case study of ombrogenous peatlands in Alberta, Canada. *Bryologist* 106, 235–245.
- Wang, M., Moore, T.R., Talbot, J., Richard, P.J.H., 2014. The cascade of C:N: P stoichiometry in an ombrotrophic peatland: from plants to peat. *Environ. Res. Lett.* 9, 024003.
- Wojtuń, B., Sendyk, A., Martyniak, A., 2013. *Sphagnum* species along environmental gradients in mires of the Sudety Mountains (SW Poland). *Boreal Environ. Res.* 18, 74–88.